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(19)(CA) **APPLICATION FOR CANADIAN PATENT** (12)

(54) Method for Manufacturing Alkylglycosides

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METHOD FOR MANUFACTURING ALKYLGLYCOSIDES

BACKGROUND

The invention relates to a method for manufacturing alkylglycosides by direct synthesis, starting with fatty alcohols and saccharides and using acid catalysts.

The term "alkylglycosides" within the framework of the invention refers to compounds in which alkyl residues are bonded acetalically to monomeric and/or oligomeric sugar residues.

The term "alkyl residues" refers to residues derived from monofunctional alcohols which can be linear or branched and preferably contain 8-20 carbon atoms. Especially suitable alkyl residues are those derived from alcohols obtained from natural substances such as fats and oils and usually constituting a mixture, having C_{12}/C_{14} chains for example, and also can have unsaturated residues.

It is known that alkylglycosides can be produced from fatty alcohols and saccharides using an acid catalyst. Numerous methods are described in the literature in which a glycoside is initially obtained from saccharides by reacting a low-molecular-weight alcohol such as methanol, ethanol, or the like, which is then converted into the desired alkylglycoside by reacetylization with a higher-molecular-weight alcohol. Numerous catalysts have been recommended for this type of reaction.

It is also known that synthesis can be performed from saccharides directly by reaction with a higher-molecular-weight alcohol, i.e. alcohols with 8 up to 22 carbon atoms, for example. Numerous acid catalysts have been mentioned in the literature for this type of reaction as well.

Thus, for example, as indicated in European Patent Application 0 132 043, inorganic acids such as hydrochloric acid, sulfuric acid, and phosphoric acid are recommended; p-toluenesulfonic acid and boron trifluoride

p-toluenesulfonic acid and boron trifluoride are also recommended for this purpose. According to the teaching of European Patent Application 0 132 043, acid anionic surfactants such as alkyl sulfates, alkylbenzolsulfonic acids, and alkylsulfonic acids are used as catalysts to manufacture alkylglycosides.

European Patent Application No. 0 415 192 recommends sulfosuccinic acid as a catalyst because this substance is readily biodegradable.

In International Patent Application WO 90/07516 strong hydrophobic organic acids are generally recommended as catalysts for manufacturing alkylglycosides. These are primarily compounds which are surfactants. In addition to alkylbenzolsulfonic acids, sulfuric acid alkyl esters, copolymers of styrene-sulfonic acids, among others, dialkyl esters of sulfosuccinic acid with a total of at least 10 carbon atoms in the alkyl groups are generally mentioned. No examples of these alkyl esters are contained in this patent application.

Although numerous catalysts have already been mentioned for indirect and direct synthesis of alkylglycosides, there is still a need for improved methods of direct synthesis which use acid catalysts.

The goal of the invention, therefore, is a method especially for direct synthesis of alkylglycosides beginning with fatty alcohols with 8-22 carbon atoms and saccharides, especially monosaccharides, using acid catalysts which is economical to perform, permits short reaction times for given reaction conditions, leads to a product with good properties, is simple to perform, and leads to reproducible results. The goal of the invention is also to provide a method which can be performed continuously and which leads to products that exhibit favorable viscosity properties, possess satisfactory solubilization, and have interface properties that are satisfactory in practice.

This goal is achieved by a method for manufacturing alkylglycosides by reacting monosaccharides

with fatty alcohols in the presence of an acid catalyst, characterized by the fact that sulfocarbonic acids with the exception of sulfosuccinic acid and/or sulfocarbonic acid esters with the exception of sulfosuccinic dialkyl esters, whose total number of carbon atoms in the two alkyl groups is at least 10, and/or anhydrides of polyvalent sulfocarbonic acids are used as the catalyst.

The sulfocarbonic acids or their esters used according to the invention can be of an aliphatic, cycloaliphatic, aromatic, or heterocyclic nature. They can contain the usual substituents. They can be sulfomono-, sulfodi-, sulfotri-, or polyvalent carbonic acids or their esters. Of the polyvalent carbonic acids, i.e. sulfodicarbonic acids, sulfotricarbonic acids, etc., mono-, di-, tri-, etc. esters can be used.

The alcohols from which the esters can be derived are those with generally 1 to 22 carbon atoms, with the alcohol being derived from aliphatic, olefinic, cycloaliphatic, and araliphatic residues.

In one especially advantageous embodiment of the process according to the invention, the esters are derived from the same fatty alcohols used as reactants in the reaction.

The following is a list of examples of acids and esters that have proven advantageous according to the invention: sulfoacetic acid and its methyl esters, sulfoacetic acid dodecyl esters, ortho-, meta-, and parasulfobenzoic acid and their alkyl esters such as methyl-, dodecyl-, tetradecyl esters, sulfosuccinic monododecyl esters, sulfosuccinic dimethyl esters, sulfopropionic acid and its dodecyl esters, sulfoisophthalic acid and its mono- or didodecyl esters, sulfophthalic acid anhydride, 5-sulfotrimellitic acid and mono-, di-, and tridodecyl esters, 4-sulfo-1,8-naphthalene dicarbonic acid dodecyl esters, and 4-sulfo-1,8-naphthalene dicarbonic acid anhydride.

As for sulfocarbonic acids with 2 or more carboxyl groups, their anhydrides may be used advantageously as well.

Instead of the above-mentioned dodecyl esters, mixtures for example of dodecyl/tetradecyl esters or hexadecyl/octadecyl esters have also been used, derived from natural products.

The quantity of catalyst can be varied within relatively wide limits, for example from 1 to 20 mmol per mol of glucose. Preferably, 2 to 10 mmol are used per mol of glucose.

In addition, mixtures of the above-defined acids with one another or mixtures of the acids with the above-mentioned esters, or finally mixtures of the esters with one another may be used. The same also applies to the anhydrides.

Glucose is preferably used as the monosaccharide, and a finely ground glucose with an average particle diameter of 3-4 µm is especially suitable.

In one especially advantageous embodiment of the method according to the invention, the reaction is performed continuously.

Direct synthesis within the framework of the invention means that the reactants, fatty alcohol and monosaccharide, are reacted directly to form alkylglycoside without the intermediate step of reacetylization of an intermediate product with a short-chain alcohol.

It was especially surprising that the invention makes it possible to provide a method in which a large number of new catalysts can be used for this purpose. The method operates very economically, is easy to perform, and offers reproducible products with adjustable properties.

It was also particularly surprising that the process according to the invention can also be performed continuously in simple fashion and produces products which, by comparison with products on the market with otherwise equivalent performance, have much lower

viscosities. This means that it is possible even at higher concentrations, to produce aqueous systems that are pumpable at room temperature. The interface tension value and the solubilization of products are outstanding; the foam stability is good as well.

It is also surprising that the catalysts, especially with continuous operation, lead to very high reaction rates. It is also surprising that according to the invention the reaction can often be performed at lower temperatures and nevertheless results in high yields. Another advantage of the invention lies in the fact that syrupy glucose can be reacted, like that obtained for example by acid or enzymatic hydrolysis of starch. These syrupy glucoses contain, in addition to glucose, in other words a monosaccharide and water, oligomers and, to a lesser extent, polysaccharides. Syrupy glucose can also be obtained from saccharose, obtained for example from sugar beets.

The invention will now be described in greater detail with reference to the following example:

General Procedure and Description of Apparatus Used

A commercial 1-liter Büchi glass reaction vessel with double-jacket heating, Intermig stirrer, bottom drain, and distillation fitting was used as the reactor.

The following examples were prepared in batch operation, i.e. all of the glucose (Glc) and all of the fatty alcohol (FA) were placed in the reactor and the mixture was raised to the required temperature with stirring and evacuation to 20 mbar.

Then the catalyst was added and this point in time was considered the beginning of the reaction.

The reaction water was removed continuously in the form of steam and precipitated in the graduated vessel. The water production rate was rated as the conversion rate of the Glc (1 mol of water was released for each mol of reacted Glc).

The time required for 99% Glc reaction was considered the reaction time and used for the comparisons.

Example

10 mmol 4-sulfophthalic acid dilauryl ester per mol of glucose was used as the catalyst.

90.5 g glucose anhydrous (Cerestar) with an average particle size of 5 µm was placed in the reactor together with 412.0 g fatty alcohol (Nafol 1214 from Condea containing approximately 54% lauryl and approximately 44% myristyl alcohol) and, after evacuation to 20 mbar, was brought to the reaction temperature of 110°C with stirring.

99% of the glucose added was reacted after 32 minutes. The reaction product was clear, white, and showed the following analytical values after separation of the FA to 1.2%:

Free glucose: < 1 wt.%

Monoglucoside (C_{12} + C_{14}):53.5 wt.%

Comparison Example

This example was prepared analogously with a catalyst according to the prior art (p-toluenesulfonic acid). For 99% glucose reaction, however, 85 minutes were required, in other words more than twice the reaction time by comparison with a catalyst according to the invention.

The reaction product was clear and light yellow in color; after FA separation to 1.6% residual content, it had the following analytical values:

Free glucose: < 1 wt.%

Monoglucoside (C_{12} + C_{14}):52.4 wt.% .

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. Method for manufacturing alkylglycosides by reacting monosaccharides with fatty alcohols in the presence of an acid catalyst, characterized by the fact that sulfocarbonic acids with the exception of sulfosuccinic and/or sulfocarbonic acid esters with the except of sulfosuccinic dialkyl esters, whose total number of carbon atoms in the two alkyl groups was at least 10, and/or anhydrides of polyvalent sulfocarbonic acids were used as the catalyst.

2. Method according to Claim 1, characterized by the fact that esters of aliphatic and/or cycloaliphatic sulfocarbonic acids are used.

3. Method according to Claim 1, characterized by the fact that esters of aromatic sulfocarbonic acids are used.

4. Method according to one of Claims 1 to 3, characterized by the fact that esters are used which are derived from aliphatic, olefinic, cycloaliphatic, and araliphatic alcohols with up to 22 carbon atoms.

5. Method according to one or more of Claims 1 to 4, characterized by the fact that sulfocarbonic acid esters are used whose alcohol component is the same as that used for reacting the fatty alcohol used as the reactant.

6. Method according to one or more of Claims 1 to 5, characterized by the fact that glucose is used as the monosaccharide.

7. Method according to Claim 6, characterized by the fact that a finely ground glucose is used.

8. Method according to Claim 7, characterized by the fact that a glucose with a particle diameter of 3 to 4 µm is used.

9. Method according to one or more of Claims 1 to 8, characterized by the fact that the reaction is performed continuously.

ABSTRACT OF THE DISCLOSURE

A method is described for manufacturing alkylglycosides by reacting monosaccharides with fatty alcohols in the presence of an acid catalyst, characterized by the fact that sulfocarbonic acid and its esters with the exception of sulfosuccinic acid and its dialkyl esters whose total number of carbon atoms in the two alkyl groups is at least 10, as well as anhydrides of polyvalent sulfocarbonic acids, are used as the catalyst.